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MAGNETIC PROPERTIES OF SOME MACROMOLECULES OF BIOLOGICAL INTEREST

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Introduction

This report outlines progress during the second three months of a basic research study. The aims of the research are to measure the magnetic susceptibility of some selected macromolecules, using a new superconducting detection system, and to correlate the results of these measurements with the structure and with the physical and chemical properties of the compounds. Of particular interest is the possibility of detecting effects due to the quantized collective motion of electrons in large organic molecules. When these molecules are subjected to high magnetic fields, their diamagnetic susceptibility may change in a way which will be related to the multiple connectivity of the molecules. These changes may give information about molecular structure and it then may be possible also to identify certain biological molecules by magnetic susceptibility measurements.

The ultimate motivation for these measurements springs from the idea expressed by Fritz London that the property of long range ordering of the momentum, which characterizes the electrons in a superconductor and results in the appearance of macroscopic quantum phenomena, may be of more

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general significance and, in particular, may be important in understanding the macromolecules of biochemistry.[1] This ordering, if present, should affect the magnetic susceptibility of the molecules, and may be detectable with the techniques being developed in this research.

A primary incentive for these measurements is the recent appearance of extremely sensitive new techniques for measuring magnetic flux. These techniques are being developed at Stanford University in conjunction with experiments on quantized magnetic flux in superconductors.[2] Together with superconducting shields and superconducting persistent current magnets, these techniques make possible entirely new kinds of magnetic measurements.

An aim of this research is to adapt the new techniques, which have sensitivity and magnetic field range potentialities much greater than existing methods, to the measurement of magnetic susceptibility.

During the second three-month period of this research, all the components of the susceptibility cryostat were completed and assembled. Experiments (at liquid helium temperatures) were conducted for approximately three weeks, to test and calibrate the apparatus. Some of the sample materials have been obtained and purified.

Magnetic Susceptibility Apparatus

The measurements being undertaken in this study will make use of a modulated inductance detector, a superconducting circuit originated at Stanford University for detecting quantized magnetic flux in superconductors. If this circuit can be adapted for susceptibility measurements, it will give much greater sensitivity than present methods and will also make possible some new types of measurements.

A. Description

The detection circuit for the susceptibility apparatus is diagrammed in Fig. 1. Two fundamental properties of superconductors are used in this circuit -- (1) the fact that the electrical resistance is zero, thus allowing persistent currents (i.e., currents that flow undiminished forever in a closed superconducting circuit), and (2) the Meissner effect, the expulsion of the magnetic field from the interior of a solid superconductor when it is cooled below its superconducting transition temperature in the presence of a magnetic field.

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[1] London, F., Superfluids, Vol. 1, p. 9. John Wiley and Sons, New York, 1950

[2] Deaver, B. S., Jr., and W. M. Fairbank, Proceedings of the Eighth International Conference on Low-Temperature Physics. R. O. Davies ed., Butterworth, Washington, D. C., 1963, p. 116

Coils L_1, L_2, and L_3 in Fig. 1 constitute a closed superconducting circuit. If the magnetic flux linking one of the coils, say L_1, is changed, an emf is generated, causing a current to flow around the loop. Since the resistance is zero, the current will persist and will induce, in coils L_1, L_2, and L_3, magnetic flux changes whose sum is just equal and opposite to the flux change made externally on L_1, thus leaving the total flux linked by the circuit (i.e., all three coils) unchanged. The persistent current is proportional to the external flux change made through L_1 and is a permanent record of that change. A measurement of this persistent current is then a measure of the flux change. If the flux change is caused by removal from L_1 of a sample magnetized by an external field, H, then the current will be proportional to the magnetization (or susceptibility) of the sample.

The persistent current is measured by using a modulated inductance detector (shown in the lower part of Fig. 1). Coil L_3 and a secondary coil, C, are wound around a superconducting post, P. The superconducting post is thoroughly grounded at one end to a temperature, T_0, below its superconducting transition temperature. The other end can be heated periodically so that the post rises above its superconducting transition temperature and then cools back to the superconducting state. When the post is normal (i.e., not superconducting), the current flowing in L_3 causes a magnetic flux to link both L_3 and C. When the post goes superconducting, the magnetic flux inside the post is expelled because of the Meissner effect, thus changing the amount of flux linking L_3 and C. As the post is heated and cooled periodically, the periodic variation of the flux in C causes an alternating voltage across the coil, C. This voltage can be measured and is proportional to the persistent current flowing in the circuit L_1-L_2-L_3.

Although in principle a single coil is sufficient for measurement of the magnetization or susceptibility of the sample, a better design uses two coils, L_1 and L_2. These coils are identical in size and number of turns. However, the windings of L_1 are made in the opposite direction to those of L_2.

The sample whose magnetization or susceptibility is to be measured is placed inside coil L_2, in the presence of a uniform magnetic field, H, applied to both L_1 and L_2. Any persistent current already present in the circuit L_1-L_2-L_3 is eliminated by momentarily heating a small region of the circuit with the switch heater, S, causing a normal resistance in that part of the circuit and thus causing all current to decay to zero. Then the heater is turned off and the circuit is allowed to return to the superconducting state.

Now the sample is moved from coil L_2 into coil L_1; since coil L_1 has its windings in the opposite direction, the change in flux in the circuit (because of the movement of the sample) is twice that which would have occurred had the sample simply been removed from coil L_2.

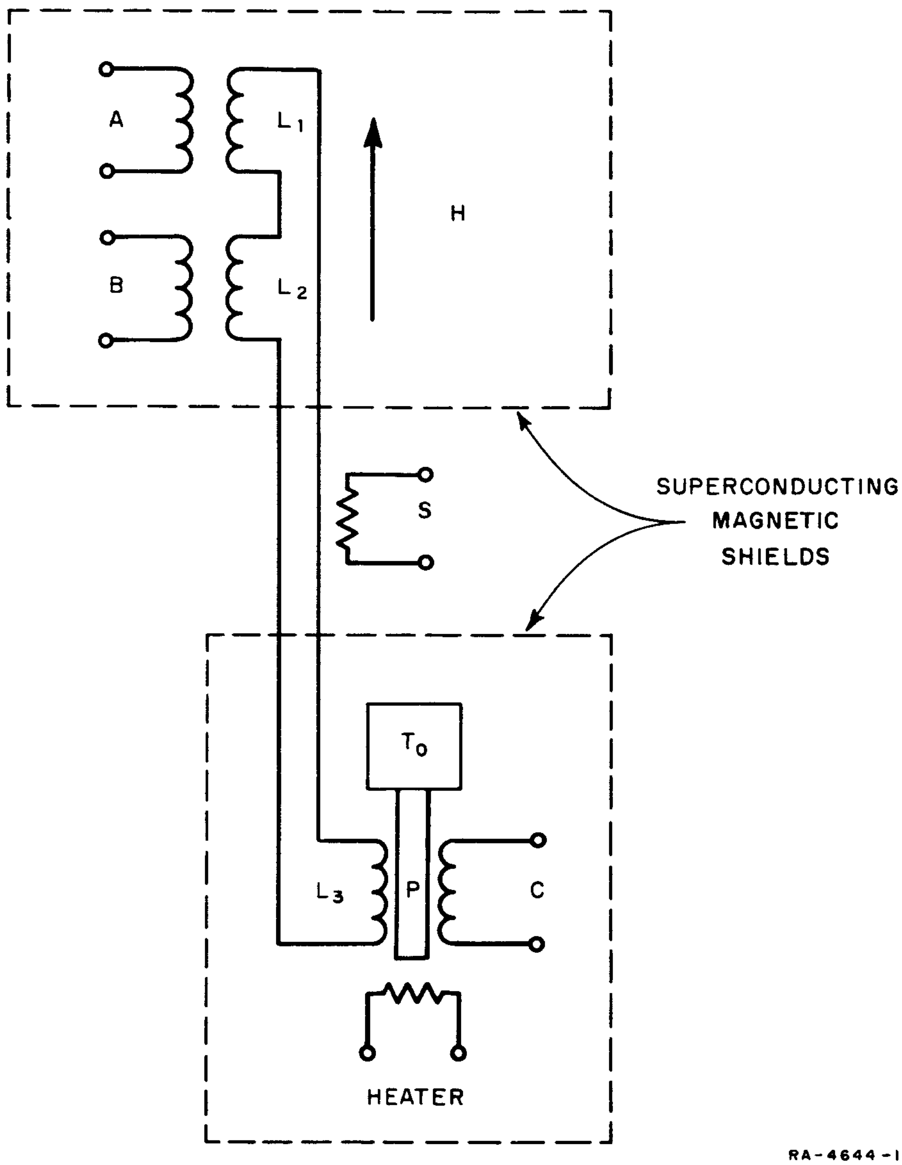

FIG. 1 DETECTION CIRCUIT

If the persistent current induced in the superconducting circuit is to measure only the magnetization of the sample, coils L_2 and L_1 must be shielded from all external magnetic field variations. These coils are therefore placed inside a superconducting magnetic shield which, because of its zero resistance, allows no change in the magnetic flux inside the shield once it has been cooled through the superconducting transition temperature. Insofar as coils L_1 and L_2 are identical in number of turns and size, any magnetic field change which is common to both coils causes no current to flow in the superconducting circuit because of the opposite direction of the windings. There are still very stringent requirements on the stability of the field, H, however, since this field may be tens of kilogauss and since field changes of approximately 10^{-5} gauss in coils L_1 or L_2 can be detected and will interfere with the susceptibility measurement for weakly diamagnetic materials. This degree of stability can be obtained only with superconducting persistent current magnets contained inside the superconducting magnetic shield.

One of the major design problems is the shielding of the modulated inductance detector (Fig. 1) from external magnetic fields. Since the detector measures all magnetic fields penetrating post P, both that due to current flowing in L_3 and that due to any external source, all external fields must be eliminated. Consequently the detector is also placed inside a superconducting magnetic shield. Before cooling the shield through its superconducting transition temperature, post P is placed in as nearly zero magnetic field as can be obtained with external ferromagnetic shields. The superconducting shield is then cooled below its transition temperature to preserve this near zero field state. A further reduction of the field is accomplished with a trimming solenoid contained inside the magnetic shield. The possibility of maintaining a near zero (say 10^{-4} to 10^{-5} gauss) region at the position of the detector while at the same time applying a field of tens of kilogauss in the region of the sample depends crucially on the shielding properties of superconductors.

In order to achieve extreme sensitivity in measuring the alternating voltage appearing across coil C by discriminating against noise, standard phase-sensitive detection techniques are used. The heater for post P is operated by an oscillator at frequency f_0 (usually between 100 and 1000 cps). Since heating of post P appears for each half of the sine wave, the voltage generated at C is at $2f_0$ and in a fixed phase relation to the heating voltage. The lock-in amplifier using a reference signal from the heater oscillator is used to observe the signal at frequency $2f_0$ from coil C at the optimum phase and is typically used with bandwidths from 1 to 1/10 cps.

An improved technique, which is actually being used, is to provide a coil, B, which is concentric with coil L_2. When the sample has been moved from L_2 to L_1, thus causing a persistent current and a voltage output at C, an opposing flux change can be introduced into coil L_2 via a current in coil B. When the flux change due to the current in B is exactly equal to the change that occurred because of the movement of the sample from L_2 to L_1, there will be zero output from coil C, and the current flowing in coil B is then a direct measurement of the magnetization of the sample. The detection circuit is then being used simply as a null detector of high sensitivity, eliminating dependence on the gain characteristics of the detection system.

The device can be calibrated either against a sample of the same size and shape with known susceptibility or by calculation from the geometry of coils B and L_2 and the size and the position of the sample.

Although superconducting shields, magnets, and detection circuit necessarily operate at liquid helium temperatures, the sample may operate at any desired temperature by placing it inside a double-walled dewar vessel. Figure 2 is a schematic diagram of the susceptibility cryostat which has been constructed. The whole assembly shown in this diagram is immersed in liquid helium. There are three independently sealed vacuum-tight chambers -- (1) the upper superconducting shield and contents, (2) the switch heater, and (3) the lower superconducting shield and detector. The upper chamber is filled with low pressure helium gas which maintains the entire contents at the temperature of the surrounding helium bath. The switch is contained in a chamber at high vacuum which allows thermal isolation so that a small portion of the superconducting circuit may be heated above its transition temperature. The detector chamber is also maintained at high vacuum so that the superconducting shield surrounding the detector may be warmed above its transition temperature and the ambient field at the superconducting post may be adjusted by external coils to be as near zero as possible.

The sample is contained inside a dewar vessel whose inner wall is a copper capillary tube 0.050 inch O.D. with a 0.003-inch wall. The outer wall is 0.100 inch O.D. beryllium-copper alloy tubing with a 0.003-inch wall thickness. These tubes are sealed at the bottom end and the region between is maintained at high vacuum. To provide additional radiation shielding the inner wall is wrapped with multiple layers of 0.00025-inch thick aluminized Mylar.

Resistors, T, are provided at the base of the sample dewar to measure the temperature and to provide heating. A small metallic conductor connects the inner wall to the outer wall and provides a small controllable heat leak. The heat input from the heater resistor maintains the sample at any desired temperature from that of the helium bath up to room temperature.

The pickup coils are wound directly on the outer wall of the sample dewar. The superconducting coils, L_1 and L_2, are wound with 0.002-inch thick x 0.020-inch wide niobium-25% zirconium ribbon and the coil, L_3, around the superconducting post, P, is wound of 0.002-inch O.D. niobium wire. The joints between the ribbon and the wire are made by spot welding to achieve a complete superconducting circuit. Coils A, B, and C consist of several thousand turns of No. 48 copper wire. Coil E is a small winding of 0.005-inch diameter bismuth wire whose magnetoresistance is used as a measure of the magnetic field. Coil D can be used together with a ballistic galvanometer to check the magnetic field value by shutting off the solenoid and observing the voltage pulse from this coil.

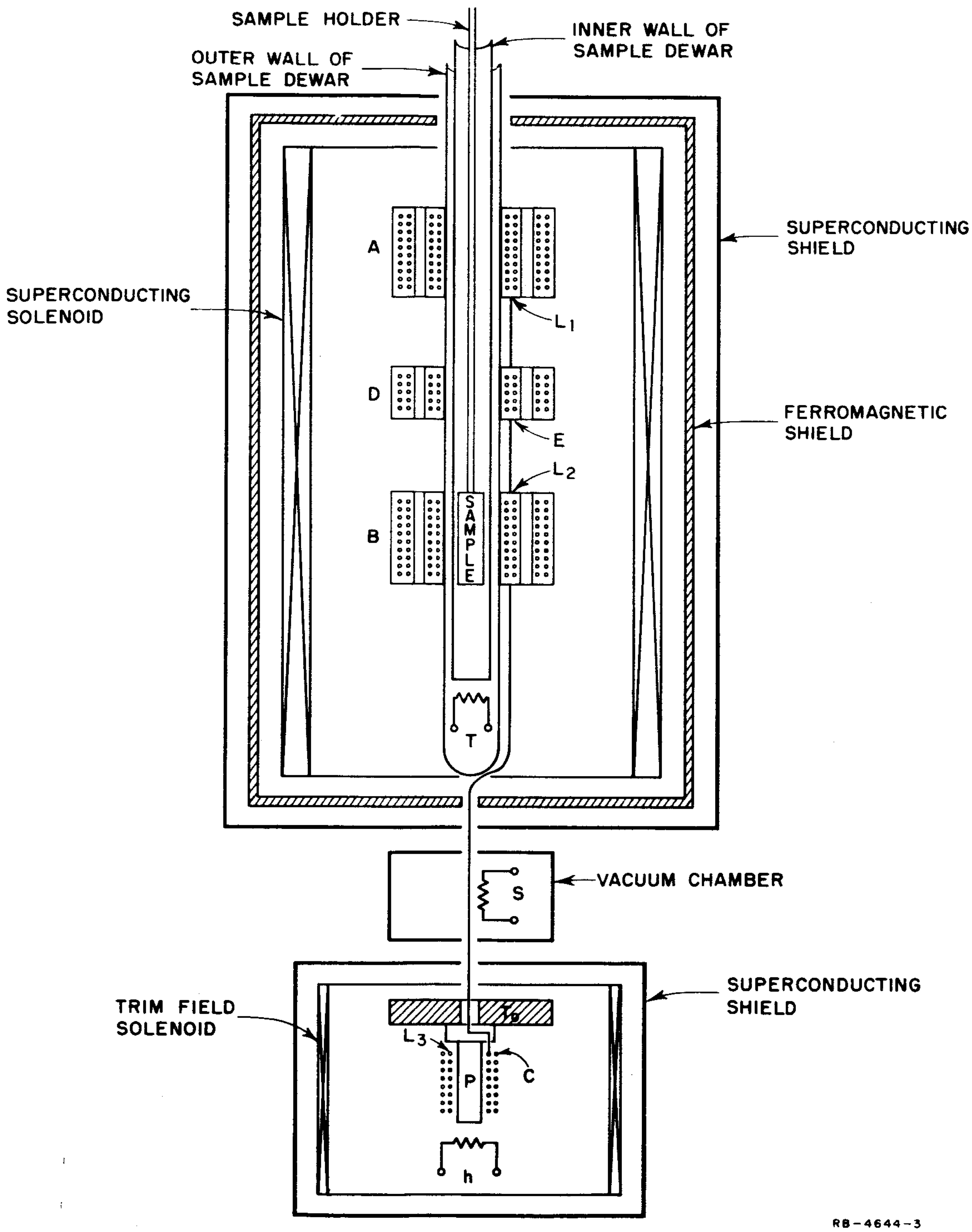

FIG. 2 SCHEMATIC DIAGRAM OF SUSCEPTIBILITY CRYOSTAT

The applied magnetic field for susceptibility measurements is furnished by a superconducting solenoid wound in two sections. The inner section consists of approximately 50,000 turns of 0.003-inch diameter niobium-25% zirconium wire and has a 3/16-inch inner diameter and approximately 1 inch outer diameter. A second winding outside this consists of 13,000 turns of 0.010-inch diameter niobium-zirconium wire. The inner coil alone can produce fields up to approximately 30,000 gauss; the outer coil can produce about 20,000 gauss. In combination the two may produce fields of approximately 40,000 gauss. These solenoids are provided with superconducting shunts which can be maintained normal while the magnets are being energized and can then be allowed to go superconducting so that the solenoids operate as persistent current magnets. A ferromagnetic can surrounds these solenoids to provide a return path for the magnetic flux lines so that the niobium-zirconium outer superconducting shield has a reduced effect on the field of the solenoid.

The sample is mounted, as shown in Fig. 3, inside a quartz capillary tubing which is evacuated after the introduction of the sample; a few millimeters of mercury pressure of helium gas are then admitted and sealed into the tube. Motion of the sample is accomplished by a stainless steel tubing connected to the brass fitting and extending out of the top of the cryostat to a rack and pinion drive permitting a very precise positioning of the sample in the two coils, L_1 and L_2. When it is in position in the sample dewar, the sample holder is surrounded with low pressure helium gas to maintain thermal equilibrium between the sample and the dewar walls.

Figure 4 is a photograph of the outer sample dewar wall with coils mounted and with a terminal block attached to its lower end. The detector post, P, shown in Fig. 5 is a 1-millimeter diameter, approximately 1 centimeter long, tin rod on which are wound coil L_3 and signal coil C. An aquadag coating at the tip is the resistive heater and a copper pedestal is the heat sink, T_0. The can, C, is the vacuum jacket surrounding the switch, S, and containing a third superconducting shield which protects the pair of superconducting leads being heated by S from any magnetic fields produced by the heater resistors. The coil assembly shown in Fig. 4 mounts directly on top of the can, C, at the opposite end from the superconducting post, P.

A view of the disassembled cryostat components is shown in Fig. 6. Superconducting magnets A and B mount inside the ferromagnetic shield C, and together with terminal block D, all mount inside the copper jacket, K. Thin-walled beryllium copper tubes, 1/8-inch in diameter, connect the magnet jacket and detector circuits to the top plate and provide access for the leads and pumpouts for the various vacuum chambers. Magnetic shield F contains switch S (shown in Fig. 2) and mounts inside the vacuum jacket, E, which in turn is mounted to the bottom of jacket K. Finally the copper pedestal, G, mounts at the bottom of can E and is covered by the superconducting shield, H, and the vacuum jacket, I, which

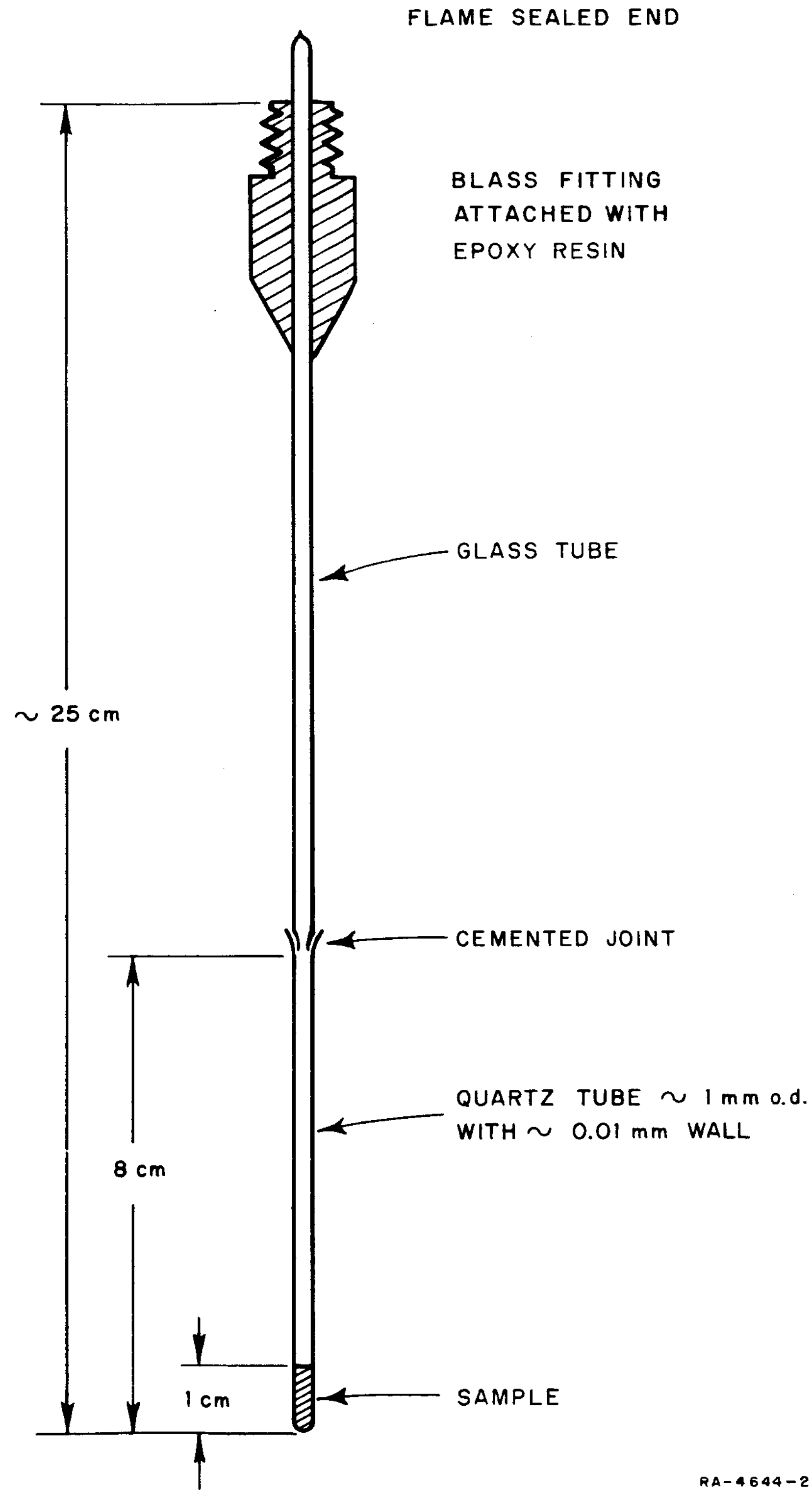

FIG. 3 SAMPLE HOLDER

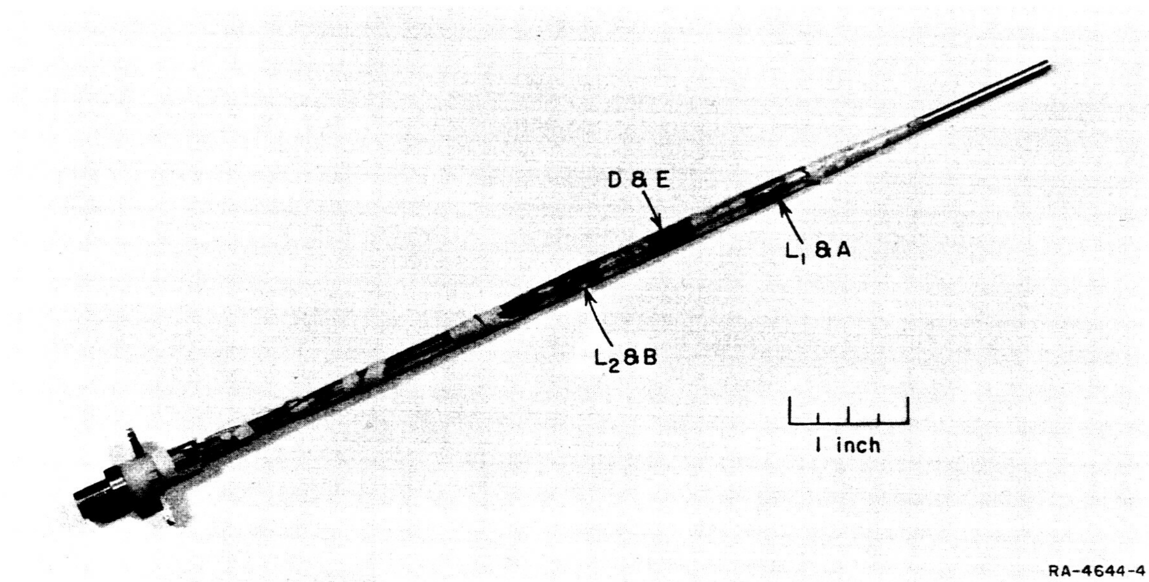

FIG. 4 SAMPLE DEWAR OUTER WALL WITH COILS MOUNTED

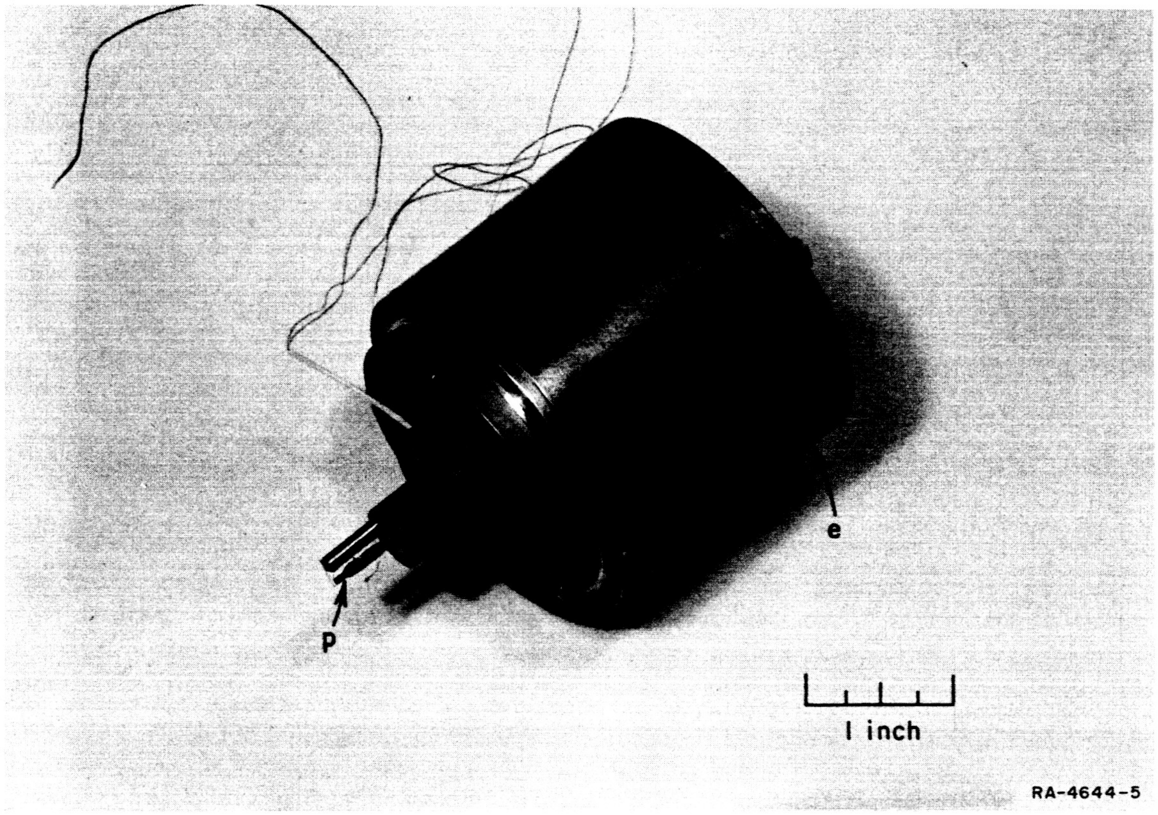

FIG. 5 MODULATED INDUCTANCE DETECTOR

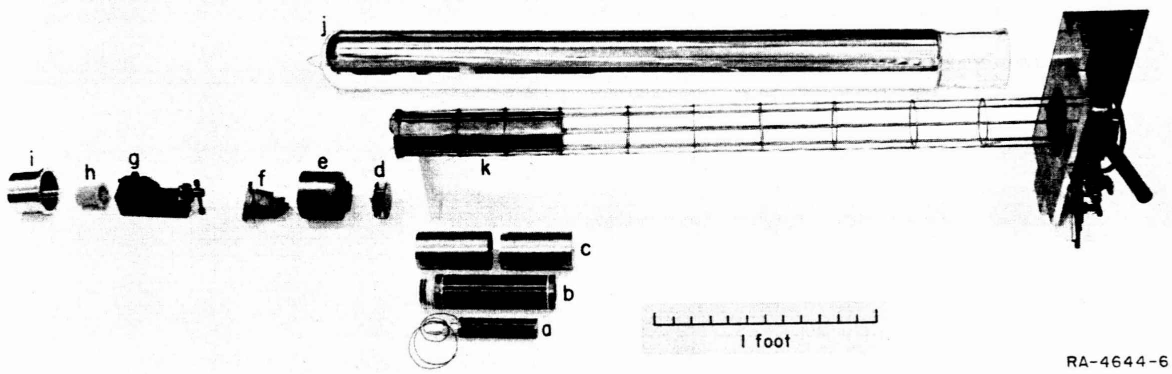

FIG. 6 CRYOSTAT COMPONENTS

screws to the bottom side of can E. The entire assembly is immersed in liquid helium inside the glass dewar, J. The liquid helium bath temperature is maintained at approximately 3.6°K by pumping through the large copper line at the back of the top plate.

The disassembled components of the sample dewar are shown in Fig. 7. As mentioned above, the inner wall of the sample dewar consists of a 0.050-inch O.D. copper capillary, C in Fig. 7, which attaches to its continuation a stainless steel tube, B, extending to the top plate of the cryostat. The outer wall of the sample dewar consists of the beryllium-copper tube shown in Fig. 4, which in turn connects to stainless steel tube A, in Fig. 7. This extends to the top plate with a pumpout (shown in Fig. 7) allowing the jacket region to be evacuated. Part E shown in Fig. 7 is the brass fitting also depicted in Fig. 3. The stainless steel tubing, D, provides the sample motion by the rack and pinion assembly shown at the far left edge of the photograph.

Figure 8 is a photograph of the cryostat in operating position with the associated pumps and electronics. Only the top plate and sample motion control show at the top of the helium dewar, which itself is immersed inside a liquid nitrogen dewar. The large Helmholtz coils were used initially to null the ambient field in the room to approximately 10^{-3} gauss at the region of the detector before the superconducting shield surrounding the detector is cooled. It has been found that a cylinder of Hypernom which slips around the base of the nitrogen can be used to reduce the ambient field to approximately the same level. Hypernom cylinders have been used in all subsequent experiments.

Although a relatively complicated-looking arrangement of electronics is assembled here, only a few simple functions are being carried out. These functions can be identified roughly with the five individual racks shown in Fig. 8. Starting at the left rear rack they are as follows:

1. Oscillator and impedance matching network for heating the superconducting post
2. A very sensitive ac resistance bridge employing a lock-in detector and used to measure the magnetoresistance of the bismuth wire (to determine the magnetic field at the sample) and to measure the resistance of various thermometer resistors in the cryostat
3. A current supply for the superconducting solenoids and current supplies for the null coil and trim fields
4. A low-noise amplifier and lock-in detector with recorder output for measuring the signal voltage from coil C
5. A magnetometer for determining the field strength at the center of the Helmholtz array

Finally there are numerous power supplies for these various components.

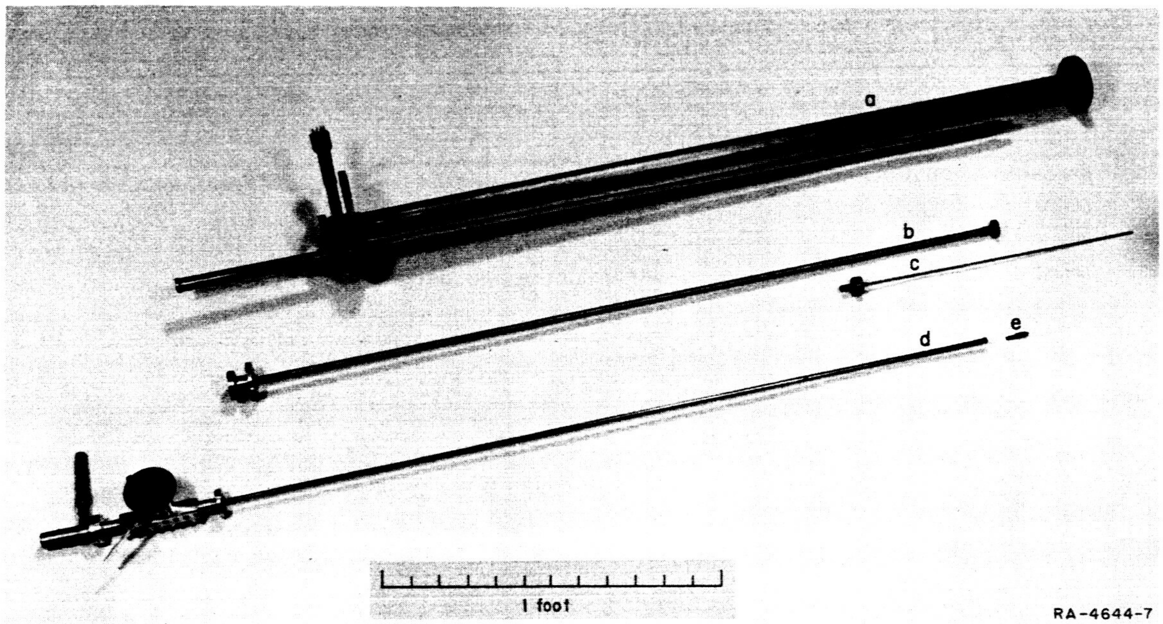

FIG. 7 SAMPLE DEWAR COMPONENTS

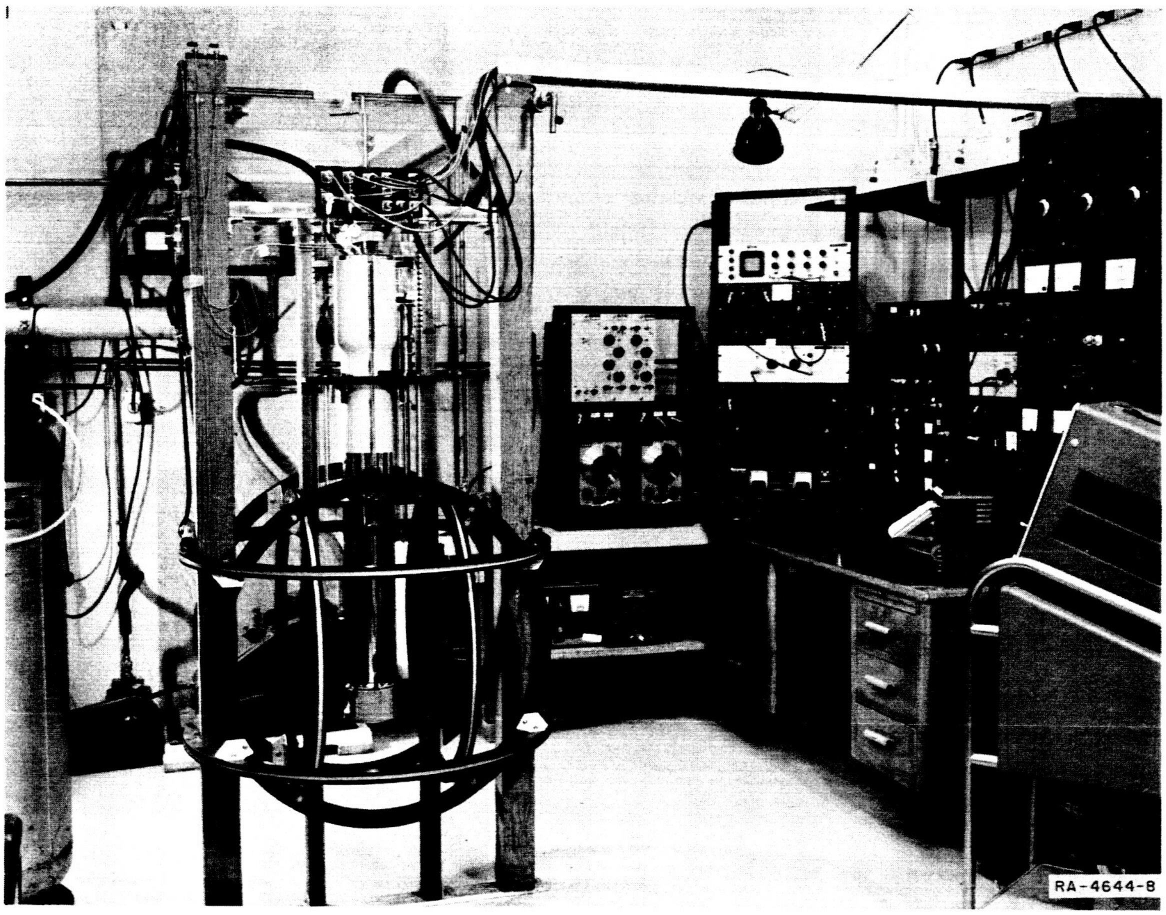

FIG. 8 COMPLETE SUSCEPTIBILITY APPARATUS

B. Operations

Immediately upon completion of the cryostat components the entire apparatus was assembled and initial liquid helium temperature runs were begun to test its performance. The detection circuit operated as designed and was sensitive to field changes of approximately 10^{-4} gauss in the pickup coils when operating at 200 cps. This limit was set by the presence of small ambient field gradient at the superconducting post and was being systematically reduced during the early runs. Adequate shielding was obtained between the sample chamber and the detection chamber at least up to a field of 25,000 gauss in the sample chamber.

The sample handling mechanism and the small sample dewar also operated properly. The sample was maintained near room temperature for a period of approximately 48 hours while the cryostat was immersed in liquid helium.

One major difficulty was encountered with the superconducting magnets during these runs. The connections to the superconducting solenoids were imperfect; this resulted in an excessive amount of heating. This heating prevented the solenoids from being operated in the persistent current mode which is necessary for susceptibility measurements. These faulty connections apparently also prevented the operation of the magnet at fields higher than 25,000 gauss. The magnets are currently being reconnected to eliminate this difficulty. An almost identical magnet was constructed previously; when tested, it was found to achieve fields of approximately 30,000 gauss and to operate in the persistent current mode.

Some additional liquid helium temperature runs were made to calibrate the various thermometers and the bismuth magnetometer as well as to develop technique in using the modulated inductance detector circuit.

Sample Selection and Preparation

A sample of coronene, $C_{24}H_{12}$, has been purified by multiple recrystallization and its purity has been checked by its ultraviolet spectrum. This material will be used for the initial susceptibility measurements. A sample of hexabenzocoronene, $C_{42}H_{18}$, has been located and should be on hand within a few weeks. Samples of etioporphyrin and deuteroporphyrin have also been obtained, as have magnesium and copper phthalocyanine. These materials will be prepared for subsequent measurements.

Dr. F. Sondheimer has indicated that he will supply us with samples of his cyclic polyenes, provided our requirements do not conflict with those of a group in England to whom he has already committed samples.

Bascom S. Deaver, Jr.

Bascom S. Deaver, Jr., Physicist
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E. M. Kinderman, Manager
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